

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 433 674 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **90122004.6**

(51) Int. Cl.⁵: **C22B 19/00**

(22) Date of filing: **17.11.90**

(30) Priority: **18.12.89 FI 896064**

(43) Date of publication of application:
26.06.91 Bulletin 91/26

(84) Designated Contracting States:
BE DE ES FR GB NL

(71) Applicant: **OUTOKUMPU OY**
Länsituulentie 7 A
SF-02100 Espoo(FI)

(72) Inventor: **Asteljoki, Jussi Akseli**
Pellilmaantie 18
SF-28400 Ulvila(FI)
Inventor: **Kojo, Ilkka V.**
Koivistonluodontie 55
SF-28330 Pori(FI)
Inventor: **Mäkinen, Juho Kaarlo**
Esikkokuja 2
SF-28450 Vanha-Ulvila(FI)

(74) Representative: **Zipse + Habersack**
Kernatenstrasse 49
W-8000 München 19(DE)

(54) **Method for producing zinc by means of iron melt reduction.**

(57) The invention relates to a method for producing zinc from oxidic zinc raw materials by reducing them in carbonaceous iron melt. In the method the zinc raw material is injected, together with a carbonaceous reducer, into the iron melt, so that the oxidic zinc is reduced and volatilized as metallic vapour. This vapour is discharged from the iron melt together with the carbon monoxide released in the reduction reaction and the carrier gas, and is conducted out of the reactor into a separate condenser, where the zinc is recovered by condensing.

EP 0 433 674 A1

METHOD FOR PRODUCING ZINC BY MEANS OF IRON MELT REDUCTION

The invention relates to a method for producing zinc from oxidic zinc raw materials by reducing them in carbonaceous iron melt. In this method the zinc raw material is injected, simultaneously with the carbonaceous reducer, into the iron melt, so that the oxidic zinc is reduced and volatilized as metallic vapour. The vapour is discharged from the iron melt together with the carbon monoxide, which is released in the reduction reaction and is conducted with a carrier gas out of the reactor into a separate condenser, where the zinc is recovered by condensing.

Nowadays the production of zinc is mainly carried out by roasting sulphidic zinc concentrate in a fluidized bed furnace at a temperature of roughly 950 °C, so that an oxidic zinc raw material, i.e. the calcine, is formed. The zinc oxide of the calcine is then dissolved into a slightly acidic electrolyte, wherefrom the zinc is recovered in electrolysis. In the roasting process there is created an amount of zinc ferrite, corresponding to the amount of iron contained in the concentrate, which ferrite does not dissolve in the first so-called weak acid leaching. Therefore the precipitate left undissolved at the first stage is dissolved at the second stage in a so-called (hot) acid leaching. There is now also dissolved a part of the iron, which must be precipitated prior to conducting the solution into electrolysis. The iron is precipitated for instance by means of a jarosite or goethite process, where the amount of produced iron residue is remarkable with respect to the slight iron content. The said iron residues are nowadays stored in waste ponds which form a potential environmental hazard owing to their heavy metals and other harmful components. The process is continued with solution purification and electrolysis. The amount of energy consumed in the process is relatively larger than the energy consumed in the production of other ordinary metals, and about twofold with respect to the theoretical energy demand. The major part of this energy required is the electric energy consumed in the electrolysis.

The major part of the pyrometallurgically produced zinc is nowadays manufactured in the so-called Imperial Smelting process from zinc and lead concentrates. In this method the sulphidic concentrate is sinter-roasted into oxide in a process which renders a lump product suitable to be used as feed in a shaft furnace. In connection with the sintering process, there are created large amounts of dusts containing lead/zinc, which are unhealthy when inhaled. The dusts and gases containing SO₂ also form a remarkable environmental hazard. The sintered roast is fed, together with hard metallurgical coke, into a shaft furnace, where the roast is heated while passing down through the shaft. The heat required by the process is produced in the bottom part of the shaft furnace by burning a part of the carbon contained in the coke by means of preheated air, while another part thereof serves as a reducer in the process. Oxidic zinc and lead are reduced in the lower part of the shaft furnace, and the lead forms a separate phase at the bottom of the furnace. Gangue minerals and the possibly added fluxes as well as the coke ashes form a molten slag on top of the lead. A prerequisite for the process is that the iron oxide contained in the slag is not reduced into iron. This sets a limit to the employed reduction potential, and certain amounts of heavy metals remain unreduced in the slag; these may limit the use of the said slag for instance as earth filling. The zinc reduced in the lower part of the furnace is volatilized and lifts, together with the CO, CO₂, H₂O, H₂, N₂ gas created in the process, countercurrent with respect to the batch, up to the top part of the furnace, wherefrom the gas is in most cases conducted to a lead splash condenser. In this condenser the gas is quickly chilled while meeting the cooler metal splash curtain, so that the reoxidation of zinc is kinetically prevented owing to the effect of the H₂O and CO₂ of the gas, and metallic zinc is dissolved into the lead. The lead is circulated out of the furnace and chilled, so that the solubility of zinc thereto is reduced and the molten zinc is separated on top of the lead layer, wherefrom it is recovered. Because lead is capable of dissolving only a small amount of zinc, the amount of lead to be circulated in the process per a given time unit must be about 400 times as much as the produced amount of zinc.

The plasmazinc method described in the articles Björklund, G., Fäldt, I., Santen, S.: Das PLASMAZINC-Verfahren für die Verwertung geringwertiger Rohstoffe; Erzmetall 34(1981)2, 77-81, and Eriksson, S.: The Plasmazinc process for recovery of zinc from primary and secondary materials; Zinc '85, 827-840, differs from the Imperial Smelting method mainly in that the heat required by the shaft furnace process is brought into the process in the form of plasma gas developed by means of electric energy. Thus the flue gases created in the process are more reducing, and theoretically the zinc can be condensed directly in a zinc bath. However, the energy consumption and costs are relatively high.

In the patent application GB-A 2,048,309 there is introduced a zinc production method where the sulphidic concentrate is smelted into a sulphidic, low-oxygen matte, wherefrom the zinc is volatilized by circulating the sulphidic matte through a vacuum. According to the said patent application, the required energy is brought to the process by means of oxidizing part of the sulphur contained in the sulphide in a

different part of the furnace, which makes it possible to produce even other metals, for instance copper. The weak spot in the process is the need to use a vacuum.

In the method of the US patent 4,741,770, the sulphidic zinc raw material is first smelted by injecting it in oxidizing conditions into a slag bath, so that the zinc is oxidized and remains in the slag. The zinc-bearing slag thus created is then reduced by means of the injection method in the second step of the process, so that the zinc is volatilized and recovered by condensing from the gas phase. A method of the same type is introduced in the patent publication AU 86 61527, but there the zinc is allowed to reoxidize into fume, which is then treated in a separate process in order to produce metallic zinc.

In the articles Abramowitz, H., Rao, Y. K.: Direct reduction of zinc sulphide by carbon and lime, Trans. Instn. Min. Metall. Section C 87C(1987) C180-188 and Ueda, Y., Nakamura, T., Noguschi, F.: Direct reduction of zinc sulphide, Met. Rev. of MMIJ, 1(1984)2, 70-83 there is described a process where sulphidic zinc concentrate is allowed to react in a raised temperature together with carbon and lime. The lime reacts with the sulphur of the zinc sulphide and there is created calcium sulphide. The created zinc oxide reacts with the carbon, and is reduced and volatilized as gas together with the carbon monoxide created in the reaction, from which gas the zinc is easily condensed without danger of reoxidation. Among the drawbacks of the method let us point out the need for external, indirectly produced energy in order to obtain heat, and the gypsum created as a side product from the reaction, the storage whereof creates a potential environmental hazard.

In the latter article, among others, there are shown calculations which prove that it is theoretically possible to reduce and volatilized zinc with a good yield into a gas phase directly from the sulphidic raw material by allowing it to react, with a precisely defined proportion of constituents, together with carbon and oxygen. Problems arise from the difficulty to condense the zinc as metallic, with a sufficiently good efficiency, from the $\text{SO}_2 + \text{CO}_2 + \text{CO}$ gas; so far this has not succeeded.

For example in the article Azakami, T., Itoh, S.: Fundamental studies of zinc extraction by the iron-reduction distillation process, Metallurgical Review of MMIJ, 5(1988)1, 55-69, there are described processes where the zinc from an oxidic zinc raw material, which in the former case consists mainly of metal industry dusts, and in the latter case of molten slag, is reduced by means of metallic, solid iron. In the Azakami process, a mixture of iron oxide and zinc oxide is first reduced at the temperature of 1000 - 1150 K by carbon monoxide, so that the iron oxides are reduced. Thereafter the temperature is raised up to 1370 K, where the oxidized iron can reduce the zinc oxide, and the zinc is volatilized as metallic gas, which then is condensed. The drawback of these methods is the indirect use of energy for maintaining the relevant temperatures, and the controlling of the amount of solid iron required in the reactions.

The US patent 4,514,221 introduces a method where a zinc roast is injected, together with carbon which is used as a reducer and energy source, and with oxygen-enriched air to a slag phase, so that the zinc oxide is reduced and volatilized as metallic vapour together with the $\text{CO} + \text{CO}_2 + \text{N}_2$ gas, wherefrom it is condensed either in a lead or zinc splash condenser. The creation of metallic iron must be avoided in this process, and therefore the zinc content of the slag phase remains fairly high, so that the slag phase requires further treatment, for instance slag fuming prior to its storage in the residue area, in order to avoid the environmental hazards caused by the dissolution of zinc.

In the above described injection-based zinc production processes the injection of the oxidic material and the reducer takes place into the slag melt. In the method of the present invention, the carbonaceous reducing material is injected, together with the oxidic zinc-bearing material, into iron melt by means of a carrier gas. Iron melt as a medium differs remarkably from slag melt, among others due to its better heat transfer and lower viscosity. Moreover, the carbon dissolved in the iron serves as a reducer and also as a carbon buffer, which stabilizes the reduction reactions if there are disturbances in the feeding. By employing iron melt as a medium there is achieved a higher smelting capacity than while using slag melt. In the method of the invention, the reduction potential can be adjusted remarkably lower than in the Imperial Smelting process, because there is no danger of the reoxidation of zinc.

In coal gasification processes the use of iron melt is a known method. The finely divided carbonaceous material, with a typical particle size below 0.1 mm, is injected by means of a carrier gas to the iron melt together with oxygen. The coal is dissolved in the iron melt and reacts with the oxygen, thus creating CO gas. The gasification of coal takes place very rapidly owing to the high temperature and carbon content of the melt. The ashes and sulphur contained in the coal form a slag on the surface of the iron melt, and part of the sulphur is discharged along with the gases. The slagging can be improved by means of fluxes. While employing oxygen as the injection gas, a large amount of heat is released in the coal burning reactions.

In the process developed by the KHD Humboldt Wedag Ag (Molten Iron Puregas Process), finely divided coke is injected to iron melt while the carrier gas is nitrogen. At the same time oxygen is blown, together with water vapour, and they react with the carbon dissolved in the iron. The obtained product is a

gas which is mainly composed of carbon monoxide and hydrogen. The ashes and sulphur of the coke, together with the flux, form a slag on the surface of the iron melt. The injection can be carried out either by means of bottom-blowing or top-blowing technique. The reported injection capacity of coke into iron melt is 250 - 500 kg/h per ton Fe.

5 The CGS process described in the DE publication 2,952,434 differs from the KHD process with regard to the way of feeding the material. Here the finely divided solids, carbon and lime (CaO) used as a slag-forming agent, are blown together with the oxygen and water vapour onto the surface of the iron melt at a high velocity.

In the articles Axelsson, C.-L., Torssell, K., Törneman, B.: Coal gasification in an iron bath, Scand. J. Metallurgy 16(1987), 214-219 and Axelsson, C.-L., Sato, K., Torssell, K., Törneman, B.: The P-CIG Process for coal gasification, Scand. J. Metallurgy 17(1988), 242-247, there are described two coal gasification processes, one of which is carried out in normal pressure (Coal Iron Gasification Process) and the other in a 3 bar overpressure (Pressurized-Coal Iron Gasification Process). In the CIG process, the finely divided coal, oxygen, slag-forming agents and water vapour are injected into the iron melt either by top blowing or 15 bottom blowing technique, and the obtained product is mainly CO and hydrogen gas. In the P-CIG process the injection takes place as a bottom blowing. By employing overpressure, the capacity can be raised and the produced gas can be used directly in certain pressurized projects. The employed slag-forming agents in the process are lime (CaO) or dolomite.

In the above described processes, solid coal is processed, by employing iron melt as a medium, mainly 20 into CO gas and thermal energy, which are used in some other process. In the method of the present invention, the carbonaceous material or gaseous reducer reduces the oxidic zinc raw material in iron melt into metallic zinc, and the heat required by the process is obtained, when necessary, from the same process by burning an excessive amount of coal with respect to the oxides reduced in the reactor. At least a part of the thermal energy required in the process can also be produced externally, either by burning the 25 created CO gas, or completely by means of an external source of energy.

In the method of the present invention, the zinc raw material which is at least partly oxidic is reduced, by means of solid or gaseous reducers, by injecting them into molten iron by means of a carrier gas. The metallic zinc is removed from the reduction step in gaseous form, along with the flue gases, and is recovered in the flue gas line in a separate condenser, by means of zinc or lead washing. The essential 30 novel features of the invention are apparent from the appended patent claim 1.

During the reduction process, in the reactor there are formed at least three phases which are separated from each other in equilibrium: a metallic melt, mostly iron, an oxidic slag and a gas phase. Depending on the composition of the feed, a sulphidic matte phase may also be formed in the reactor.

The raw material of the reduction process is a finely divided material, typically made of zinc 35 concentrate by means of roasting. In the said method it is also possible to treat oxidic or partly oxidized metallic residue and side product materials, which are crushed to a suitable particle size. The employed reducer is typically finely divided, i.e. <0.1 mm, coke, coal dust or peat coke. The use of gaseous reducers, typically hydrocarbons such as natural gas, is also possible.

Depending on the mainly oxidic, non-reducible gangue minerals brought to the process by the feed 40 materials, which are oxidic zinc raw material and reducer, suitable fluxes can be added to the feed in order to adjust the fluidity and other properties of the resulting slag. Such additives are typically lime (CaO) and sand (SiO₂).

The process is carried out in a reactor of the closed type, where to the raw materials are injected, solid materials by means of a carrier gas. The injection is advantageously carried out below the surface of the 45 iron melt, either by using a separate injection lance, or by intermediation of the tuyeres of the reactor. The iron melt serves as a medium for the heat and material transfer in the reduction reactions, and the iron contained in the feed, as well as the non-volatile side components which are reduced in the reaction, are dissolved to the iron melt in the stationary state of the process. Part of the iron is let out of the reactor in batches. The slag phase formed in the reaction is treated in a similar fashion.

50 Because the dissolution of carbon to iron lowers its melting point, the reduction process of zinc oxide can be carried out below the melting point of pure iron. The reduction temperature is limited by the molten range of the iron-carbon system, which is largest with high carbon activities, $a_{\text{C,gral}} > 0.5$, and thus the process is typically operated within the temperature range 1300 - 1500 °C.

The heat energy required by the process is produced either by means of indirect heating, or by burning 55 in the reducing reactor an excessive amount of coal or another reducer with respect to the reducible oxides of the feed.

The recovery of gaseous zinc, or zinc vapour, is carried out in a flue gas line by means of a conventional lead or zinc washer, where the zinc is dissolved in a known fashion to a lead or zinc

suspension which is colder than the gas flow. In certain conditions the zinc can also be condensed by direct cooling.

Because the reduction of the iron oxides in the method of the present invention does not limit the reducing capacity of the process, the modest amount of slag created in the process contains only a slight amount of heavy metals. The said heavy metals are in the slag bound in a glassy phase, and are therefore in a form only slightly soluble to water, and the said slag can be used for instance as land filling material. Thus the process does not produce residues which might cause potential environmental hazards, such as the jarosite from the electrolytic zinc production.

In the method of the present invention, the raw materials need not be sintered in order to create good strength. Thus the process does not result in such dust and sulphur hazards to the environment as are typical of the sintering processes.

In the following the method is described with reference to two examples.

EXAMPLE 1

15

The method of the present invention was applied to laboratory-scale experiments for manufacturing metallic zinc. A finely divided zinc roast was injected, together with coke powder, into carbon-saturated iron melt. The zinc oxide contained in the roast was reduced in the iron melt into metallic zinc, and was simultaneously volatilized. The volatile zinc was recovered from the gas in a separate condenser, and the obtained product was metallic zinc.

The major equipment in the experiment comprised a feed apparatus for the solid material, a melting crucible as well as a condenser connected thereto by means of gas piping. The melting crucible was located in an induction furnace, whereby the energy needed in the process was produced. The iron melt, mass 2.3 kg, was kept at a temperature of 1400° C, and the employed melting crucible was an Al₂O₃ crucible.

The injection of the roast/coke mixture into the iron melt was carried out by means of a graphite lance with an interior diameter of 8 mm, and the employed carrier gas was nitrogen (5 dm³/min). The amount of injected roast was 200 g, and the amount of injected coal dust was 30g, the injection period being 60 min. The analyses of the feed materials are presented in table I.

30

Table I: Analyses of the feed materials

	Roast	Coke
	%	%
35		
	Zn	57.0
40	Fe	8.0
	Pb	1.6
	Al ₂ O ₃	0.34
45	CaO	2.1
	MgO	0.26
	SiO ₂	0.46
	S	1.1
50	H ₂ O	4.1
	C _{fix}	2.1
	Volat.	0.10
55		89.7
		1.7

The composition of the iron melt during injection remained nearly unchanged, and the dissolution of zinc thereto was extremely slight. The composition of the melt before and after the injection is presented in

table II.

Table II: The composition of iron melt before (I) and after (II) the injection

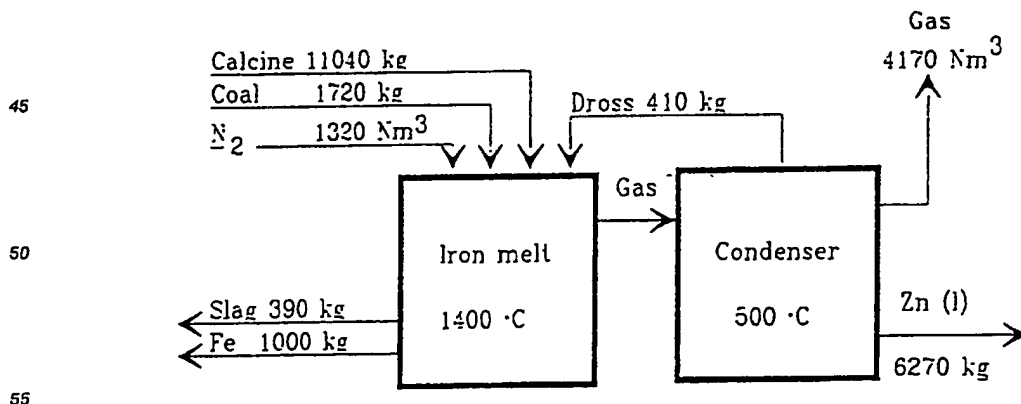
	(I)	(II)
	%	%
Fe	89.0	87.0
Zn	<0.01	<0.01
Pb	0.01	0.02
C	4.0	4.2

As a result from the reduction reactions, the zinc was volatilized into the gas phase. The gas was conducted, along the gas piping, into the condenser, where the gas was cooled down to 500 °C, so that the zinc was condensed and could be separated from the gas. The obtained final product was metallic zinc. The composition of the metallic zinc was 98% Zn. In addition to this, the zinc contained as impurities some dissolved lead and small amounts of oxidic components, which in this laboratory-scale experiment were brought to the product along with dusts.

The non-reduced components contained by the roast formed a thin slag layer on top of the iron melt. The main component in the slag was SiO₂, about 45-60%. Other components in the slag were CaO, Fe, FeO, Al₂O₃, MgO, MnO and Cr₂O₃. The zinc content in the slag was 0.1-1.5 % Zn, and the lead content was <0.1 % Pb.

EXAMPLE 2

Example 2 presents the material balance for the process of the present invention. This material balance is based on a yearly output of 50,000 tons of zinc. The employed carrier gas in the injection was hydrogen (1 Nm³/10 kg solids). The approximated zinc yield in the condensing is 95%, while the rest goes into the oxidic dross, which is recirculated to the process. The dross is mainly composed of the oxides of zinc and lead, as well as the iron entered into the process along with dust. The initial materials are the same as in example 1. The material balance is calculated according to feed per hour. The material flows are illustrated in a flow sheet:



Iron oxides, which form the major part of the gangue minerals in the roast, are reduced in the process,

and therefore the produced amount of slag is very small, only about 3.5% of the amount of fed roast. The amount of carbonaceous iron created in the process is 1000 kg/h. The slag and iron compositions according to the thermodynamic balance are the following:

5					
		Slag		Iron	%
		%			
10		CaO	19.3	Fe	88.3
		MgO	15.2	C	2.7
		Al ₂ O ₃	21.1	Si	1.6
15		SiO ₂	44.4	Zn	0.4
		FeO	0.1		
		ZnO	0.05		

20 The obtained zinc product contains about 1.9% Pb, wherefore it must be further raffinated in order to produce SHG zinc, for instance by means of a distillation process. The gas discharged from the condenser contains about 68% carbon monoxide CO, while the rest of the gas is mainly nitrogen which is used as carrier gas in the injection. Owing to its high thermal value, the said gas can be used for producing energy
25 for instance in the preheating of the batch, or for indirect heating of the reactor.

Claims

- 30 1. A method for producing metallic zinc from zinc-bearing raw materials, **characterized** in that the zinc raw material is fed, together with a reducer, into an iron melt, so that the reducer reduces the zinc raw material into metallic zinc, which is volatilized and discharged in gaseous form, and is then recovered in a condenser.
- 35 2. The method of claim 1, **characterized** in that the reducer is a finely divided carbonaceous material.
3. The method of claim 2, **characterized** in that the reducer is finely divided coke.
4. The method of claim 2, **characterized** in that the reducer is finely divided coal.
- 40 5. The method of claim 2, **characterized** in that the reducer is finely divided peat coke.
6. The method of claim 1, **characterized** in that the reducer is gaseous in form.
7. The method of claim 6, **characterized** in that the reducer is natural gas.
- 45 8. The method of claim 1, **characterized** in that the zinc raw material is oxidic.
9. The method of claim 1, **characterized** in that part of the zinc raw material consists of oxidic residue and side product materials.
- 50 10. The method of claim 1, **characterized** in that part of the zinc raw material consists of partly oxidized, metallic residue and side product materials.
11. The method of claim 1, **characterized** in that the heat needed in the process is obtained by burning in
55 the reactor an excessive amount of the reducer with respect to the oxides reduced in the process.
12. The method of claim 1, **characterized** in that the heat required in the process is produced externally.

13. The method of claim 1, **characterized** in that the reducer and the zinc raw material are injected to below the surface of the iron melt by means of an injection lance.

5 14. The method of claim 1, **characterized** in that the reducer and the zinc raw material are injected to below the surface of the iron melt by intermediation of tuyeres.

15. The method of claim 1, **characterized** in that the reduction process is carried out within the temperature range of 1300 - 1500 °C.

10

15

20

25

30

35

40

45

50

55



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 2004

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A,D	GB-A-2 048 309 (UNIVERSITY OF BIRMINGHAM) ---		C 22 B 19/00
A,D	US-A-4 741 770 (B.S. ANDREWS et al.) ---		
A,D	US-A-4 514 221 (S. GOTO) ---		
A,D	FR-A-2 445 364 (SUMITOMO METAL INDUSTRIES) ---		
X	EP-A-0 007 856 (SOCIETE MINIERE ET METALLUR- CIQUE DE PENARROYA) * claim 1, page 12, line 6 * ---	1	
A	DE-A-3 019 066 (ARBED) * claims 1,2 * ---	1	
A	EP-A-0 085 153 (KLÖCKNER-WERKE) * claim 1, page 4, lines 9-16 * ---	1	
A	US-A-2 473 611 (S. ROBSON) * claim 1 * ---	1	
A	DE-A-2 042 444 (BECHTEL INTERNATIONAL) * claims 1,7 * -----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 22 B
Place of search		Date of completion of search	Examiner
Berlin		17 December 90	SUTOR W
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone			
Y: particularly relevant if combined with another document of the same category			
A: technological background			
O: non-written disclosure			
P: intermediate document			
T: theory or principle underlying the invention			
E: earlier patent document, but published on, or after the filing date			
D: document cited in the application			
L: document cited for other reasons			
&: member of the same patent family, corresponding document			